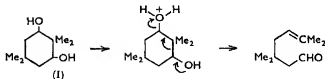


**436. Alicyclic Diketones and Diols. Part II.\* The Dehydration of *cis*- and *trans*-2 : 2 : 5 : 5-Tetramethylcyclohexane-1 : 3-diol.**

By A. W. ALLAN, R. P. A. SNEEDEN, and (in part) J. M. WILSON.

Dehydration of *cis*- and *trans*-2 : 2 : 5 : 5-tetramethylcyclohexane-1 : 3-diol with potassium hydrogen sulphate has been shown to give 1 : 1-dimethyl-3-isopropylidenecyclopent-2-ene, 2 : 3 : 5 : 5-tetramethylcyclohexanone, and 2 : 2 : 5 : 5-tetramethylcyclohex-3-enol. Syntheses of 1 : 1-dimethyl-3-isopropylcyclopentane, 2 : 3 : 5 : 5-tetramethylcyclohex-2-enone, and 2 : 2 : 5 : 5-tetramethylcyclohexanol are described. The formation of the dehydration products is discussed with reference to the conformations of the diols.

THIS work was undertaken in order to establish whether a suitably substituted cyclic 1 : 3-diol (I) might,<sup>1</sup> by analogy with acyclic compounds,<sup>2</sup> undergo dehydration to the unsaturated open-chain aldehyde, thus:



The preparation of pure *cis*- and *trans*-2 : 2 : 5 : 5-tetramethylcyclohexane-1 : 3-diol (I) has already been described,<sup>3</sup> and dehydration of either of these compounds with potassium

\* Part I, *J.*, 1958, 557.

<sup>1</sup> Cf. English, Russel, and Bratcher, *J. Amer. Chem. Soc.*, 1950, **72**, 1653.

<sup>2</sup> English and Bratcher, *ibid.*, 1952, **74**, 4280.

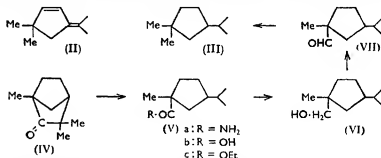
<sup>3</sup> Allan, Sneed, and (in part) Colvin, *J.*, 1958, 557.

hydrogen sulphate gave an oil and water. In both cases the infrared spectrum indicated that the oil consisted of a mixture of an unsaturated hydrocarbon, a carbonyl compound, and an alcohol. Attempted separations based on the preferential removal of the carbonyl compound were unsatisfactory. Chromatography of the reaction product, with *iso*-pentane as the initial solvent, effected separation into a hydrocarbon, a ketone, and an alcohol. A comparison of the infrared spectra and the retention times on vapour-phase chromatography showed that identical hydrocarbons, ketones, and alcohols were obtained from both diols. The percentages by weight present in the oil were:

	<i>trans</i> -Diol	<i>cis</i> -Diol
Unsat. hydrocarbon .....	53	88
Ketone .....	30	} 12
Alcohol .....	17	

The hydrocarbon  $C_{10}H_{16}$  was rapidly oxidised in air and was shown to contain two double bonds by catalytic reduction to the saturated hydrocarbon  $C_{10}H_{20}$ . It was thus a *cycloalkadiene*. It did not give a crystalline adduct with maleic anhydride, but the ultra-violet spectrum ( $\lambda_{\max}$ , 243 m $\mu$ ;  $\epsilon$  12,500) indicated the presence of a conjugated diene system with only one double bond in a ring. Further, its infrared spectrum (see p. 2189) and the isolation of acetone (as 2:4-dinitrophenylhydrazone) after ozonolysis indicated structure (II). This was confirmed when it was shown that the derived saturated hydrocarbon was identical with 1:1-dimethyl-3-*isopropylcyclopentane* (III) prepared by the annexed route.

The structure of fencholamide (Va), the product obtained by the action of sodamide on fenchone,<sup>4</sup> has been rigorously established.<sup>5</sup> Semmler<sup>4</sup> converted it into the aldehyde (VII) by the route (Va, b, c), (VI), and (VII). In the present work many improvements were made on this synthesis. Thus the amide, which resists normal hydrolysis, was converted smoothly and rapidly into the acid by nitrous acid;<sup>6</sup> lithium aluminium hydride reduced the acid to the alcohol in excellent yield. Attempts to convert the alcohol into the hydrocarbon (III) by reduction of the toluene-*p*-sulphonate with lithium aluminium hydride<sup>7</sup> or by conversion into the chloro-compound and subsequent reduction,<sup>8</sup> led to products contaminated with unsaturated material. However, chromic acid oxidised the alcohol, giving the aldehyde and, since the latter underwent rapid oxidation in air, it was isolated as its semicarbazone. This was reduced to pure 1:1-dimethyl-3-*isopropylcyclopentane* (III) by the Wolff-Kishner method. The identity of this substance



and the hydrocarbon  $C_{10}H_{20}$  was established by a comparison of their infrared spectra and their refractive indices, and they showed identical "cracking-patterns" in the mass spectrometer.\*

\* Specimens of hydrocarbon obtained by Huang-Minlon reduction of the aldehyde gave infrared spectra which were almost identical with that of the hydrocarbon  $C_{10}H_{20}$ , but their "cracking-patterns" in the mass spectrometer indicated substantial quantities of impurities.

<sup>4</sup> Semmler, *Ber.*, 1906, **39**, 2578.

<sup>5</sup> Bouveault and Levallois, *Bull. Soc. chim. France*, 1910, **7**, 683, 736, 807.

<sup>6</sup> Cf. Carter and Slater, *J.*, 1946, 130.

<sup>7</sup> Cf. Birch and Dean, *J.*, 1953, 2477.

<sup>8</sup> Cf. Komppa and Klamt, *Ber.*, 1935, **68**, 2001.

The ketone  $C_{10}H_{18}O$ , purified through its oxime, showed no selective ultraviolet absorption, but the ultraviolet spectrum of its 2:4-dinitrophenylhydrazone (see p. 2190) indicated<sup>9</sup> that it was probably a substituted cyclohexanone, and this was confirmed by the infrared spectrum of the ketone ( $\nu_{\max}$  1705  $\text{cm}^{-1}$ , six-membered ring ketone). The most probable structure for the ketone is therefore 2:3:5:5-tetramethylcyclohexanone (VIII). The ketone was converted into the corresponding  $\alpha\beta$ -unsaturated ketone by bromination and subsequent dehydrobromination with 2:4-dinitrophenylhydrazine in acetic acid.<sup>10</sup> The 2:4-dinitrophenylhydrazone obtained in this way was identical with that of synthetic 2:3:5:5-tetramethylcyclohex-2-enone (IX). Since it can be assumed that the above reactions proceed without rearrangement, the structure of the ketone  $C_{10}H_{18}O$  is thereby established as (VIII).



2:3:5:5-Tetramethylcyclohex-2-enone (IX) was prepared by the action of methylmagnesium iodide on the methyl enol ether (X) and treatment of the product with acid. The pure ketone prepared in this way showed  $\lambda_{\max}$  244  $\text{m}\mu$  ( $\epsilon$  15,200) whereas Conia<sup>11</sup> records  $\lambda_{\max}$  247  $\text{m}\mu$  ( $\epsilon$  9600) for the same substance prepared by the methylation of isophorone. A direct comparison of the 2:4-dinitrophenylhydrazones of our ketone with that prepared from Conia's ketone indicated that the two derivatives were identical.

The alcohol fraction gave, on chromatography, a crude crystalline alcohol whose infrared spectrum indicated the presence of a hydroxyl group and a *cis*-double bond. The unsaturated alcohol was purified as its hydrogen phthalate, and owing to the small quantities available this was reduced catalytically. The only catalyst to effect reduction was platinum oxide, with the result that the uptake was far in excess of 1 mol. (presumably owing to concomitant hydrogenation in the phthaloyl residue). Hydrolysis of the reduction product furnished a crystalline saturated alcohol  $C_{10}H_{20}O$  (purified through its hydrogen phthalate) identical with a synthetic specimen of 2:2:5:5-tetramethylcyclohexanol (XI). It follows that the unsaturated alcohol must be 2:2:5:5-tetramethylcyclohex-3-enol (XII).

3:3-Dimethylcyclohexanone (XIII), prepared by a new method, was methylated with methyl iodide in the presence of sodamide, the crude product being purified as its semicarbazone. The ketone (XIV) on reduction with lithium aluminium hydride gave the tetramethylcyclohexanol (XI). It is assumed that the methylation occurs at position 2 since treatment of dihydroisophorone with isopentyl formate in the presence of base gives the 2-hydroxymethylene compound as sole product.<sup>12</sup> Further, the original diol (I) could not give rise to a cyclohexyl compound with a substituent in the 6-position.

With the structure of the dehydration products established it is of interest to consider their formation in terms of the conformations of the original diols. The *trans*-diol can only have the conformation (XV), or its mirror image, whilst the *cis*-diol can have either the conformation (XVI) (both hydroxyl groups equatorial) or (XVII) (both hydroxyl groups axial). The infrared spectrum of the *cis*-diol, in carbon tetrachloride solution, showed only one band in the hydroxyl region ( $\nu_{\max}$  3635  $\text{cm}^{-1}$ ); the *trans*-diol had  $\nu_{\max}$  3637  $\text{cm}^{-1}$ . It follows that the *cis*-diol, in contrast to *cis*-cyclohexane-1:3-diol,<sup>13</sup> is free from internal hydrogen bonding, and that the preferred conformation is the diequatorial (XVI). This

<sup>9</sup> Cf. Braude and Jones, *J.*, 1945, 498.

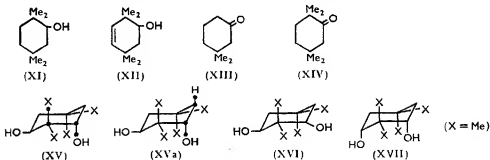
<sup>10</sup> Cf. Mattox and Kendal, *J. Amer. Chem. Soc.*, 1948, 70, 882.

<sup>11</sup> Conia, *Bull. Soc. chim. France*, 1954, 690.

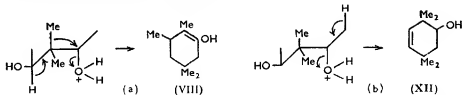
<sup>12</sup> Ruzicka, Shinn, and Seidel, *Helv. Chim. Acta*, 1940, 23, 935.

<sup>13</sup> Kuhn, *J. Amer. Chem. Soc.*, 1952, 74, 2492.

is probably due to the fact that in the diaxial form (XVII) the "1:3-interaction" of the hydroxyl groups and the axial 5-methyl group renders this form less stable than the diequatorial one. The formation of the rearranged product (II) can readily be explained,



since in both diols the steric arrangements are propitious for dehydration accompanied by ring contraction.<sup>14</sup> That the *trans*-diol yields substantial quantities of the ketone (VIII) and the alcohol (XII), can be related to the fact that in this compound there must be two other "four-body planar systems" (XV) and (XVa), not normally present in the *cis*-diol (XVI). Dehydrations involving the axial hydroxyl group would lead by scheme (a) to the ketone, and by scheme (b) to the alcohol.



Similarly the formation of small quantities of the ketone (VIII) and the alcohol (XII) on dehydration of the *cis*-diol can be regarded as arising from reactions involving the diol in the less stable diaxial conformation (XVII). It is of interest that no product indicative of ring fission was detected. Since completion of this work, Brutcher and Cenci<sup>15</sup> have reported that the dehydration of *cis*- and *trans*-cyclohexane-1:3-diol with potassium hydrogen sulphate gives a mixture of cyclohexane derivatives and no open-chain compound.

#### EXPERIMENTAL

The rotations and ultraviolet absorption spectra were taken for ethanol solutions, and all the m. p.s are corrected. The intensities of the infrared absorption bands are indicated qualitatively by the symbols s (strong), m (medium), and w (weak).

**Dehydration of *cis*- and *trans*-2:2:5:5-Tetramethylcyclohexane-1:3-diol.**—*General method.* The crushed diol (4 g.), mixed with freshly fused potassium hydrogen sulphate (8 g.) and kieselguhr (2 g.), was packed in a combustion tube and covered with a mixture of freshly fused potassium hydrogen sulphate (4 g.) and kieselguhr (1 g.). The tube, in a horizontal position, was connected to a receiver (cooled in acetone-carbon dioxide), and the apparatus was evacuated at the water-pump. The end of the tube containing the reaction mixture was heated at 170–190° for 5 hr. The receiver was then disconnected and the product purified.

***trans*-Diol.** The dried product (3.2 g.) in isopentane was chromatographed on alumina. Elution with isopentane gave 1:1-dimethyl-3-isopropylidenecyclopent-2-ene (II) (1.70 g.), b. p. 28–30°/1.7 mm.,  $n_D^{20}$  1.4730 (Found: C, 87.9; H, 12.0.  $C_{10}H_{14}$  requires C, 88.2; H, 11.8%).  $\lambda_{max}$  243 ( $\epsilon$  12,500),  $\nu_{max}$  (thin film) 1620, 1600 (w, diene system), 1370, 1360 (s,  $-CMe_3$ ), 816 (s,  $C=C$ ), and 768  $cm^{-1}$  (s, *cis*  $-CH=CH-$ ). Elution with ether gave 2:3:5:5-tetramethylcyclohexanone

<sup>14</sup> Barton, J., 1953, 1027 and references cited therein.

<sup>15</sup> Brutcher and Cenci, *Diss. Abs.*, 1958, 18, 393.

(VIII), purified as its *oxime*, prisms [from light petroleum (b. p. 60–80°)] (1.07 g.), m. p. 136–137° (Found: C, 71.0; H, 11.15; N, 8.2.  $C_{10}H_{18}ON$  requires C, 71.0; H, 11.3; N, 8.3%). The latter on hydrolysis with dilute hydrochloric acid gave the *ketone* (0.87 g.), b. p. 52–54°/1.5 mm.,  $n_D^{25}$  1.4510 (Found: C, 77.6; H, 11.5.  $C_{10}H_{18}O$  requires C, 77.9; H, 11.8%). The 2:4-dinitrophenylhydrazones crystallised from ethanol as red prisms, m. p. 132–134° (Found: C, 57.4; H, 6.5; N, 16.7.  $C_{18}H_{22}O_4N_4$  requires C, 57.5; H, 6.6; N, 16.8%),  $\lambda_{max}$  229 ( $\epsilon$  18,700), 265 ( $\epsilon$  10,500), and 361  $m\mu$  ( $\epsilon$  23,200). Elution with ether-methanol gave an oil from which the unsaturated alcohol (XII) was isolated.

*cis-Diol*. Chromatography of the dried product (2 g.) gave the diene (II) (1.8 g.) and the ketone (VIII), with infrared spectra identical with those of the compounds obtained from the *trans*-diol. There was also obtained a third fraction from which the alcohol (XII) was isolated.

*Hydrogenation of the Diene*  $C_{10}H_{18}$ .—The diene (II) (0.88 g.) in acetic acid solution over Adams catalyst (100 mg.) absorbed 312 c.c. of hydrogen (2 mol.). Neutralisation with sodium hydroxide solution, followed by distillation of the dried hydrocarbon layer, gave 1:1-dimethyl-3-isopropylcyclopentane, b. p. 148–149°,  $n_D^{20}$  1.4267 (Found: C, 85.2; H, 14.6.  $C_{10}H_{20}$  requires C, 85.6; H, 14.4%).

*Ozonolysis of the Diene*  $C_{10}H_{18}$ .—The diene (II) (1.0 g.) in pure anhydrous ethyl acetate (17 c.c.), at –75°, was subjected to a stream of ozone. When all had reacted ( $\frac{1}{4}$  hr.), as indicated by the tetranitromethane test, the solution was evaporated at 2 mm., water (10 c.c.) was added, and the whole heated under reflux for 2 hr. before distillation. After neutralisation of the distillate with sodium hydroxide solution, the neutral products and water were co-distilled directly into a solution of 2:4-dinitrophenylhydrazine (2 g.) in ethanol (50 c.c.) containing concentrated sulphuric acid (20 c.c.). The crude 2:4-dinitrophenylhydrazone (1.72 g.), m. p. 94–95°, was chromatographed on a column of bentonite (120 g.) and kieselguhr (30 g.) to give, by elution with chloroform, an unidentified 2:4-dinitrophenylhydrazone (0.345 g.), m. p. 162–165°, as red prisms (from ethanol), and by elution with chloroform-methanol (10:1) acetone 2:4-dinitrophenylhydrazone (0.722 g.) as yellow needles (from ethanol), m. p. and mixed 124–125°.

(+)-Fencholamide (Va).—(+)-Fencholamide was prepared by the action of freshly prepared sodamide [(from sodium (14 g.)] on fenchone (100 g.),  $[\alpha]_D^{25} + 69.0^\circ$  ( $c$  1.45), by Semmler's method.<sup>4</sup> The pure amide (125 g.) crystallised from methanol as plates, m. p. 100–101°,  $[\alpha]_D^{25} + 1.4^\circ$  ( $c$  2.09). For this substance von Braun and Jacobs<sup>16</sup> record m. p. 116°, and state "the amide is optically inactive;" Wallach<sup>17</sup> records m. p. 94° and "a low positive rotation;" Semmler<sup>4</sup> reports m. p. 94° and makes no mention of the rotation.

(+)-Fencholic Acid.—A saturated solution of sodium nitrite (70 g.) in water [final total volume (150 c.c.)] was added with stirring to a cooled solution of (+)-fencholamide (125 g.) in concentrated sulphuric acid (600 c.c.). The reactants were warmed on the water-bath until evolution of nitrogen ceased. Water was added to the cooled solution, and the products were extracted with ether. The acid which was isolated by extraction with sodium hydroxide solution, acidification, and extraction with ether gave on distillation (+)-fencholic acid (60 g.), b. p. 116–118°/0.5 mm.,  $n_D^{25}$  1.4558,  $[\alpha]_D^{25} + 3.97^\circ$  ( $c$  7.6) (lit.,<sup>17</sup> b. p. 151–152°/17 mm.,  $n_D^{20}$  1.4563,  $[\alpha]_D^{25} + 4.17^\circ$ ).

(+)-Dihydrofenchyl Alcohol (VI).—(+)-Fencholic acid (54 g.) in dry ether (500 c.c.) was added slowly to a suspension of lithium aluminium hydride (29 g.) in dry ether (600 c.c.), and the whole heated under reflux for 2 hr. The product isolated in the usual manner gave, on fractionation, the alcohol (VI), b. p. 84°/0.5 mm.,  $n_D^{25}$  1.4560,  $[\alpha]_D^{20} + 12.25^\circ$  ( $c$  4.65) (Found: C, 77.1; H, 12.9. Calc. for  $C_{10}H_{20}O$ : C, 76.9; H, 12.9%) (lit.,<sup>4</sup> b. p. 100°/11 mm.,  $n_D$  1.4566).

(+)-Dihydrofencholaldehyde (VII).—(+)-Dihydrofenchyl alcohol (5 g.) in benzene (50 c.c.) was added to potassium dichromate (5 g.) in water (55 c.c.) containing concentrated sulphuric acid (6 g.) and shaken vigorously for 4 hr. under carbon dioxide. Fractional distillation of the washed and dried ( $MgSO_4$ ) organic layer gave the aldehyde (VII) (2.65 g.), b. p. 50–54°/0.5 mm.,  $n_D^{25}$  1.4460 (lit.,<sup>4</sup> b. p. 80–85°/10 mm.,  $n_D$  1.4455). The semicarbazone was obtained from benzene as needles, m. p. 152–153° (Found: C, 62.2; H, 10.1. Calc. for  $C_{11}H_{14}ON_4$ : C, 62.5; H, 10.0%) (lit.,<sup>4</sup> m. p. 144–145°). The 2:4-dinitrophenylhydrazone crystallised from ethanol as red prisms, m. p. 123–124° (Found: C, 57.6; H, 6.7; N, 16.5.  $C_{18}H_{22}O_4N_4$  requires C, 57.5; H, 6.6; N, 16.8%).

<sup>16</sup> von Braun and Jacobs, *Ber.*, 1933, 66, 1461.

<sup>17</sup> Wallach, *Ann.*, 1910, 369, 63.

(+)-1:1-Dimethyl-3-isopropylcyclopentane (III).—The semicarbazone (3.36 g.) of the aldehyde (VII) was heated slowly with potassium hydroxide (7.5 g.) until nitrogen was evolved (200°). This temperature was maintained until all the hydrocarbon had distilled (1 hr.). Distillation of the product, after it had been washed with dilute sulphuric acid and dried, gave the hydrocarbon (III), b. p. 148—149°,  $n_D^{21}$  1.4240,  $[\alpha]_D^{20} + 2.94^\circ$  (c 1.46). The infrared spectra of this and the hydrocarbon  $C_{10}H_{20}$  were superposable.

*Bromination and Dehydrobromination of the Ketone (VIII).*—The ketone (0.320 g.) in acetic acid (10 c.c.) was treated slowly with bromine (1 mol.) in acetic acid. The colourless solution was treated with 2:4-dinitrophenylhydrazine (0.388 g.) also in acetic acid, and the reactants were warmed on the steam-bath for 5 min. The product, m. p. 173—174°, obtained by precipitation with water, gave on recrystallisation from ethanol 2:3:5:5-tetramethylcyclohex-2-enone 2:4-dinitrophenylhydrazone (0.14 g.) as red plates, m. p. 175—177°, alone or admixed with a specimen prepared as below (Found: C, 57.8; H, 6.1; N, 16.7.  $C_{14}H_{20}O_4N_4$  requires C, 57.8; H, 6.1; N, 16.9%).

3-Methoxy-2:5:5-trimethylcyclohex-2-enone (X).—This ether, obtained by the action<sup>18</sup> of excess of diazomethane on 2:5:5-trimethylcyclohexane-1:3-dione, crystallised from light petroleum (b. p. 60—80°) as prisms, m. p. 55—58° (Found: C, 71.25; H, 9.8.  $C_{10}H_{16}O_2$  requires C, 71.4; H, 9.6%).

2:3:5:5-Tetramethylcyclohex-2-enone (IX).—The enol ether (X) (3.2 g.) in dry ether (10 c.c.) was added slowly to a freshly prepared solution of methylmagnesium iodide [from magnesium (1.86 g.) in dry ether (15 c.c.) and heated under reflux for 6 hr. (experiments at 0° and at room temperature were not successful)]. Fractional distillation of the product, isolated in the usual manner, gave the ketone (IX) (1.5 g.), b. p. 65—67°/18 mm.,  $n_D^{19}$  1.4830 (Found: C, 79.0; H, 10.6. Calc. for  $C_{10}H_{16}O$ : C, 78.9; H, 10.6%).  $\lambda_{max}$  244 m $\mu$  (e 15,200) [lit.,<sup>11</sup> b. p. 90°/8 mm.,  $n_D^{21}$  1.4798,  $\lambda_{max}$  247 m $\mu$  (e 8600)]. The 2:4-dinitrophenylhydrazone crystallised from ethanol as red plates, m. p. 175—177°, alone or mixed with either the derivative prepared as above or with the derivative of Conia's ketone;<sup>11</sup> the infrared spectra of the three specimens were superposable.

*Isolation of the Third Dehydration Product.*—Several combined third fractions (1.63 g.) (see above, purification of the dehydration product) were chromatographed on alumina to give: (i) by elution with light petroleum (b. p. 40—60°) a mixture (0.17 g.) of ketone (VIII) and an alcohol; (ii) by elution with light petroleum (b. p. 40—60°)-ether (5:1) a crystalline alcohol (0.51 g.); and (iii) by elution with ether-methanol a mixture (0.73 g.) of the alcohol and unchanged diol (identified by its infrared spectrum). The infrared spectrum of the alcohol of m. p. 44—45°,  $\nu_{max}$  3240 (s, OH), 1710 (w, C=O in 6-membered rings), and 768 cm.<sup>-1</sup> (s, cis -CH=CH-), indicated that it was unsaturated and contained a trace of ketone. The hydrogen phthalate of (XII) crystallised from acetic acid as prisms, m. p. 153.5—154.5° (Found: C, 71.5; H, 6.85.  $C_{14}H_{22}O_4$  requires C, 71.5; H, 7.3%). This derivative (0.93 g.) was hydrogenated in ethanol solution over Adams catalyst (0.1 g.), the hydrogenation being stopped after absorption of 3.6 mols. of hydrogen. Water (3 c.c.) and potassium hydroxide (3 g.) were added to the filtered solution and the whole was heated under reflux for 3 hr. The product, isolated with the aid of ether, was converted into its hydrogen phthalate, which on recrystallisation from aqueous acetic acid gave the 2:2:5:5-tetramethylcyclohexyl hydrogen phthalate (cf. XI) as prisms, m. p. 168.5—170.5° (Found: C, 71.4; H, 8.1.  $C_{14}H_{24}O_4$  requires C, 71.0; H, 7.95%). This derivative with aqueous potassium hydroxide (10 c.c. of 10%) and subsequent sublimation of the product gave 2:2:5:5-tetramethylcyclohexanol (XI), prisms, m. p. 54—56° (Found: C, 76.6; H, 13.2.  $C_{10}H_{18}O$  requires C, 76.9; H, 12.9%).

5:5-Dimethylcyclohex-2-enone.—3-isobutoxy-5:5-dimethylcyclohex-2-enone (60 g.), prepared from dimedone by the method of Eschenmoser *et al.*,<sup>19</sup> b. p. 76°/0.1 mm.,  $n_D^{18}$  1.4810 (Found: C, 73.45; H, 9.8.  $C_{12}H_{20}O_2$  requires C, 73.4; H, 10.3%), was reduced with lithium aluminium hydride (5 g.) in ether to give, by the usual isolation procedure, 5:5-dimethylcyclohex-2-enone, b. p. 76°/16 mm.,  $n_D^{21}$  1.4699 (lit.,<sup>20</sup> b. p. 75°/15 mm.,  $n_D^{20}$  1.4710). The 2:4-dinitrophenylhydrazone crystallised from ethanol as red prisms, m. p. 161—163° (Found: C, 55.5; H, 5.35; N, 18.4.  $C_{14}H_{18}O_4N_4$  requires C, 55.25; H, 5.3; N, 18.4%).

3:3-Dimethylcyclohexanone (XIII).—The above ketone (5 g.) in ethanol (50 c.c.) was

<sup>18</sup> Cf. Born, Pappo, and Szmuszkovicz, *J.*, 1953, 1779.

<sup>19</sup> Eschenmoser, Schreiber, and Julia, *Helv. Chim. Acta*, 1953, 36, 482.

<sup>20</sup> Frank and Hall, *J. Amer. Chem. Soc.*, 1950, 72, 1645.

hydrogenated over 10% palladised charcoal (0.5 g.). Hydrogen (1 mol.) was rapidly absorbed and fractionation of the filtered solution gave the ketone (XIII), b. p. 44–45°/1.5 mm.,  $\nu_{\max}$  1710  $\text{cm}^{-1}$  (s, C=O in a 6-membered ring).

2:2:5:5-Tetramethylcyclohexanone (XIV).—The ketone (XIII) (2.82 g.) in dry ether (10 c.c.) was added to a freshly prepared suspension of sodamide [(from sodium (1.03 g.)] in dry ether (30 c.c.) and heated under reflux for 1½ hr. Methyl iodide (7.35 g.) in an equal volume of dry ether was added slowly with stirring to the cold solution, and the whole subsequently heated under reflux for 4 hr. The product (3.3 g.), isolated in the usual manner, was shown, by vapour-phase chromatography, to contain an impurity. The semicarbazone was prepared and repeated crystallisation from benzene-ethanol finally gave the semicarbazone (1.82 g.) of the ketone (XIV) as prisms, m. p. 198.5–201.5° (Found: C, 62.7; H, 10.5.  $\text{C}_{11}\text{H}_{21}\text{ON}_3$  requires C, 62.5; H, 10.0%). This on hydrolysis with dilute mineral acid gave 2:2:5:5-tetramethylcyclohexanone (XIV) (1.3 g.), b. p. 98°/46 mm.,  $n_D^{20}$  1.4448 (Found: C, 77.2; H, 11.65.  $\text{C}_{10}\text{H}_{18}\text{O}$  requires C, 77.9; H, 11.8%). The 2:4-dinitrophenylhydrazones crystallised from chloroform-ethanol as red plates, m. p. 169–171° (Found: C, 57.2; H, 6.65.  $\text{C}_{16}\text{H}_{22}\text{O}_4\text{N}_4$  requires C, 57.5; H, 6.6%).

2:2:5:5-Tetramethylcyclohexanol (XI).—The ketone (XIV) (0.88 g.) in dry ether (10 c.c.) was added to a suspension of lithium aluminium hydride (0.5 g.) in dry ether (25 c.c.) and heated under reflux for 1 hr. The product isolated in the usual manner gave, on distillation, 2:2:5:5-tetramethylcyclohexanol, m. p. and mixed m. p. 52–54°. The infrared spectra of this and the specimen prepared as above were superposable. The hydrogen phthalate crystallised from ethanol as prisms, m. p. 169.5–171.5°, alone or mixed with the specimen obtained above, and the infrared spectra of the two specimens were superposable.

One of us (A. W. A.) is indebted to the Department of Scientific and Industrial Research for a maintenance allowance. Some of the infrared spectra were determined by Dr. G. Eglinton and his associates and the analyses were kindly carried out by Mr. J. M. L. Cameron and his associates. The authors also thank Dr. R. I. Reed and Mr. W. Sneddon for obtaining and interpreting the mass-spectral data, and Professor J. Conia for the generous gift of a specimen of his 2:3:5:5-tetramethylcyclohex-2-enone.

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[Received, February 2nd, 1959.]